Recovery of Critical Metals From Superalloy Scrap by Matte Smelting and Hydrometallurgical Processing

By Gary L. Hundley and D. L. Davis

UNITED STATES DEPARTMENT OF THE INTERIOR

BUREAU OF MINES

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

°C	degree Celsius	*M*	molar mass
cm	centimeter	mL	milliliter
g	gram	mV	millivolt
g/L	gram per liter	pct	percent
h	hour	vol pct	volume percent
kg	kilogram	wt pct	weight percent
lb	pound		

RECOVERY OF CRITICAL METALS FROM SUPERALLOY SCRAP BY MATTE SMELTING AND HYDROMETALLURGICAL PROCESSING

By Gary L. Hundley[1] and D. L. Davis[2]

ABSTRACT

As part of the U.S. Bureau of Mines program to reduce the Nation's reliance on foreign supplies for critical metals, a procedure was devised to separate and recover critical metals from mixed and contaminated superalloy scrap. The process uses both pyrometallurgical and hydrometallurgical methods to treat the scrap. The mixed scrap is converted to a matte containing 4 to 7 pct S by adding S directly to the molten metal. This matte is then granulated and ground to a minus 35-mesh particle size and leached with an HCl-Cl_2 solution. This process takes essentially all the Ni, Co, Cr, Fe, Al, and Mo into solution in a 3-h leach, leaving W, Ta, Ti, and Nb (Cb) in the residue. The Mo is recovered from the chloride leach solution by solvent extraction, and the Cr and Fe are recovered together by precipitation. The Ni and Co can be recovered individually by an existing solvent extraction-electrowinning process. The W is recovered by a caustic leach of oxidized Cl_2 leach residue.

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INTRODUCTION

The United States relies on imports to meet its needs for critical and strategic metals such as Ni, Cr, and Co. To reduce this dependence on imports, the U.S. Bureau of Mines investigated methods for recovering these metals from superalloy scrap. It is estimated that approximately 55 million lb of clean and contaminated superalloy scrap was processed in 1986. Of this 55 million lb, approximately 70 pct (38.5 million lb) was recycled into the same superalloy, 20 pct (11 million lb) was downgraded, and 10 pct (5.5 million lb) was sold to refineries (*1*).[3] The 20 pct that is downgraded is contaminated, too complex, or generally not suitable to be recycled directly back into alloy production. Presently, the downgraded material is used in iron and steel production or is exported. This research sought to devise a procedure to recover these critical metals from the scrap so that they may be reused in superalloy production or as the pure metals.

The chemical and physical properties of superalloys make processing to separate and recover the metals a difficult, complex process. Not only are the superalloys high-temperature, refractory materials, but mixed alloys contain a large number of elements that must be separated.

Numerous processes have been proposed to recover and recycle the critical metals in mixed and/or contaminated superalloy scrap. These processes basically fall into two types: (1) pyrometallurgical processing and (2) hydrometallurgical processing. Pyrometallurgical processing is not very selective and generally results in a master alloy containing Ni, Co, Fe, and possibly Cr. The alloy results from melting the scrap and then oxidizing the bath to remove the more reactive metals to a slag. Hydrometallurgical methods can be very selective and can result in the recovery of pure metals. These processes use a chlorine (Cl_2) leach or a sulfuric acid leach. Brooks (*2*), Hougen (*3*), and Redden (*4*) have proposed processes that use a chlorinated HCl leach to take turnings and borings or grinding wastes into solution.

Leaching rates of bulk superalloy scrap are slow unless the materials already have a small particle size, such as the materials used in the studies mentioned above. Studies conducted by Atkinson (*5-6*) and by Laverty (*7*) addressed the problem of reducing the particle size of bulk scrap to a size that would allow rapid leaching rates. These procedures involved dissolving the scrap in molten Al or molten Zn. The former resulted in the formation of brittle intermetallic compounds that were easily crushed and that reacted rapidly with leaching solutions. This procedure had the disadvantage of also consuming the Al while processing the scrap. The method of dissolving the scrap in Zn involved distilling the Zn from a solidified melt to form a high-surface-area, friable product. This material then could be readily leached with an HCl-O_2 system. The energy requirement to distill the Zn may prevent the use of this procedure, however. Laverty also found that atomizing the scrap in air or Ar resulted in a product that leached slightly better with HCl-O_2 than the Zn-treated scrap did. The atomized scrap did not leach in the Cl_2-O_2 system, however.

Studies conducted by deBarbadillo (*8*) combined pyrometallurgical, minerals beneficiation, and hydrometallurgical techniques. In this procedure, a sulfide matte was produced by adding elemental S to molten superalloy scrap. The solidified matte was easily crushed, and then conventional minerals beneficiation techniques were applied to produce a Ni-Co-rich phase free of most of the Cr, and a Cr-rich phase. The Cr-rich phase contained a significant amount of Ni, however. The Ni-Co-rich phase was treated by a hydrometallurgical process to produce electrolytic Ni and Co. The Cr-rich phase was treated by a pyrometallurgical process to produce a Cr-Ni alloy. Unfortunately, this alloy contained a significant portion of the Ni and was not as desirable a product as pure Cr. A variation of the procedure of deBarbadillo was developed by Thomas (*9-10*). In this procedure, a sulfide matte was formed and then crushed and ground to a suitable particle size. No minerals beneficiation techniques were applied to the crushed matte. The matte was selectively leached with an aqueous HCl-Cl_2 system at a controlled oxidation-reduction potential (ORP). This procedure left most of the Cr in the leach residue, and the rest of the valuable metals were recovered from the leach solution. This process also had the undesirable result of recovering a Cr product that was contaminated with Ni.

The study presented in this report is an extension of the work conducted in the studies described above (*8-10*). The formation of a matte was used to convert the scrap to a form that could be readily ground to a particle size suitable for leaching, and to convert the scrap to a form that was more reactive toward the chloride leach solution. Leaching of sulfides with a chloride system has been conducted by several researchers and is a consistent, well-documented procedure (*11-12*). Instead of physically separating the phases in the matte or selectively leaching the matte as in the work described above, this study concentrated on a nonselective leach of the entire matte. The resulting leach solution was then treated to recover individual metals.

[3]Italic numbers in parentheses refer to items in the list of references at the end of this report.

PROCEDURES AND RESULTS

Figure 1 shows a simplified flowsheet of the process developed in this study. Briefly, the procedure consisted of melting the superalloy scrap, adding S to form a matte of the desired S level, and granulating the matte in a water-jet granulator. The granulated matte was ground to the desired particle size in a rod mill and then leached with an HCl-Cl_2 leach solution. The leaching step took essentially all the Ni, Co, Cr, Fe, Mo, and Al into solution, leaving the W, Ta, Ti, and Nb (Cb) in the residue. Following solid-liquid separation, the solid residue was treated with hot perchloroethylene to remove the free S generated in the leach. Sulfur was recovered from the organic solvent by cooling the hot solvent. The S-free leach residue was heated in air to oxidize the sulfides and then was leached with a strong sodium hydroxide (NaOH) solution to remove the W. The Ti, Ta, and Nb were left behind in the solids. The leach solution from the HCl-Cl_2 leach was treated with trioctyl phosphate to extract the Mo and a portion of the Fe. The Mo and Fe could be stripped from the organic phase with a dilute HCl solution. The leach solution, after the Mo was removed, was treated with NaOH solution to raise the pH from 1.0 to approximately 2.5. Precipitation at 100° C resulted in a poorly filterable precipitate, and the Cr-Fe removal was not as complete. Also, some Ni and Co were removed in the precipitate with the latter procedure. To solve this problem, the solution was heated in an autoclave at 200° C to precipitate essentially all of the Cr and Fe as a readily filterable product. A ferrochrome product could be created from this precipitate by reduction and could be further processed to high-purity Cr if that was the desired product. Converting ferrochrome to high-purity Cr involves converting the ferrochrome to an ammonium chrome alum by reaction with sulfuric acid and ammonium sulfate, followed by electrolysis (*13*). The leach solution, which at this point contained basically Ni and Co, would be treated with a commercial solvent extraction-electrowinning (SX-EW) procedure used at Falconbridge Nikkelverk A/S, Kristiansand, Norway (*14*).

PREPARATION OF MATTES

The same composite superalloy composition used by deBarbadillo (*8*) was used in these studies. A synthetic master alloy was used to simulate mixed superalloy scrap rather than using actual scrap, so that a consistent feed material was available for the test work. The master alloy was formed by melting the individual metals together in an induction furnace. The composition of this alloy was determined from the composition of typical superalloys and the relative quantities of each type that are produced. This composition, in weight percent, was 14.5 Cr, 60.0 Ni, 10.0 Co, 5.0 Fe, 4.5 Mo, 2.0 W, 1.5 Ta, 1.0 Nb, 1.0 Al, and 1.0 Ti. The mattes were formed by melting the metal in a graphite crucible in an induction furnace and adding elemental S. A total metal weight of 12.6 kg was used in most of the tests to form mattes. The molten alloy was heated to 1,450° C, and S was added directly to the melt. The S was formed into cylinders 5 cm in diameter by 5 cm tall by pouring molten S into molds and allowing it to solidify. The desired amount of S was added to the molten bath a cylinder at a time and was stirred into the bath with a graphite rod. Sulfur retention in the matte ranged from approximately 75 to 95 pct, depending on the total S level in the matte. Low-S mattes, as expected, had a greater S retention. Mattes produced had S levels ranging from 2.8 to 33.7 pct.

After a matte was formed, it was treated in one of two ways. In the first procedure, the matte was poured into a conical mold and allowed to cool slowly. The solidified matte then was crushed and ground in a rod mill to produce the desired particle size. The crushing and grinding became more difficult as the S level in the matte decreased. The material became much tougher and harder to grind at low S levels. Mattes with S contents above about 15 pct were brittle and relatively easy to grind.

The second procedure was to granulate the molten matte in a water-jet granulator. This produced a friable, easy-to-grind material. Mattes of all S levels were granulated. Samples of mattes that had been slow-cooled were remelted and granulated to compare the leaching characteristics of the two procedures. When the S level in the matte was decreased to the 4- to 7-pct range, even the granulated material became difficult to grind to a smaller particle size. Improvement in the granulating process may result in a material that requires no further grinding, but time did not permit further study of the granulating process.

PHASE RELATIONSHIPS IN THE NICKEL-CHROMIUM-SULFUR SYSTEM

The structure of various mattes was determined by examination with X-ray diffraction and scanning electron microscope (SEM) microprobe methods. There were three major phases present in the mattes: a nickel sulfide (Ni_3S_2) phase, a metallic Ni phase, and a chromium sulfide phase. Either the Ni_3S_2 phase or the metallic Ni phase was continuous, depending on the overall S level in the matte. The other two phases were dendritic in nature and were dispersed throughout the continuous phase. The

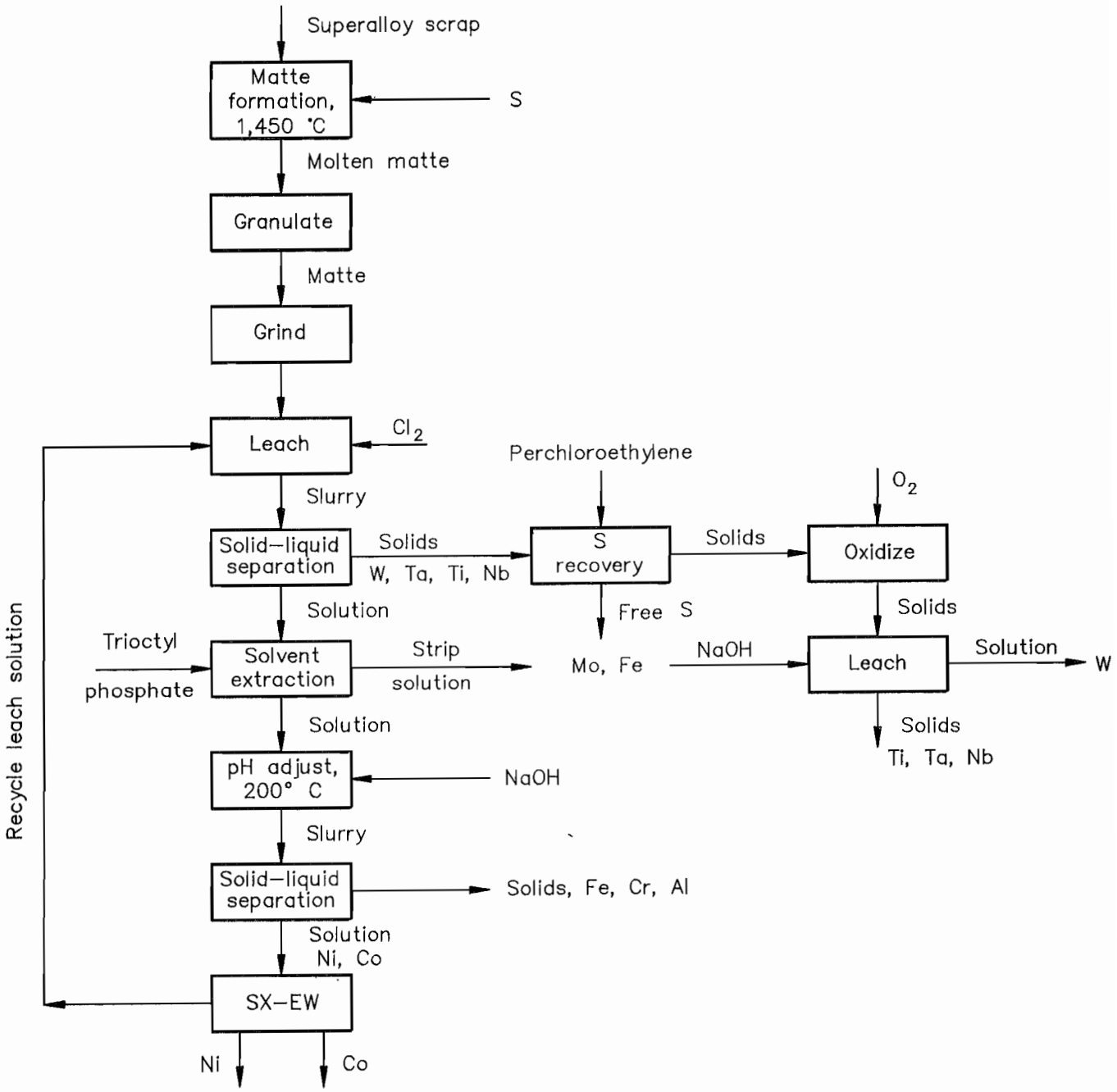

Figure 1.—Flowsheet for metal recovery from superalloy scrap.

metallic Ni phase was continuous at S levels of 5 to 10 pct. As the S level increased, more Ni_3S_2 formed, until it became the continuous phase. The Ni_3S_2 phase contained a small amount of Fe and Co, but no Cr was found. The metallic phase contained a significant amount of Fe and Co and a small amount of Cr. The chromium sulfide phase contained a significant amount of Ni and Co, with a small amount of Fe. The chromium sulfide phase had either a Cr_5S_6 composition with 10 to 15 pct Ni dispersed in the matrix or a $NiCr_2S_4$ composition with a spinel structure. Most of the minor elements, such as Mo, W, Ta, and Nb, exist in separate subphases, either as a sulfide or in the metallic state. The phases present and their approximate compositions are shown in table 1 for two mattes, one containing 25.7 pct S and the other containing 15.9 pct S.

LEACHING STUDIES

Leaching tests were conducted on a batch basis using a beaker on a hot plate with the contents stirred by a propeller-type mixer. Chlorine gas was sparged into the solution using a fritted glass bubbler. Most tests were conducted using 500 mL of solution and 50 g of solids. The ORP of the solution was measured with a combination Pt versus Ag-AgCl electrode. Most tests were conducted at a temperature of 95° C. The leach solution contained 2*M* HCl and had a copper chloride ($CuCl_2$) concentration ranging from 0 to 60 g/L Cu ion. The Cu ion was added to increase the leaching rate. The Cu acts as a Cl_2 carrier through the cuprous-cupric ion couple. In addition, the leach solution contained nickel chloride ($NiCl_2$), with an Ni ion concentration of 80 g/L. The Ni was added to the solution because commercial SX-EW operations recycle this much Ni in the leach solution. Tests at different Ni levels showed that this concentration of Ni in the leach solution did not affect the extractions obtained. Chlorine gas was bubbled into the solution at a rate creating a final ORP of 260 to 800 mV. The major chemical reactions involved in leaching the Ni are shown below.

$$Ni_3S_2 + 3Cl_2 \rightarrow 3Ni^{2+} + 6Cl^- + 2S^o. \quad (A)$$

$$2Cu^+ + Cl_2 \rightarrow 2Cu^{2+} + 2Cl^-. \quad (B)$$

$$Ni_3S_2 + 2Cu^{2+} \rightarrow 2NiS + Ni^{2+} + 2Cu^+. \quad (C)$$

$$NiS + 2Cu^{2+} \rightarrow Ni^{2+} + 2Cu^+ + S^o. \quad (D)$$

The mattes were ground and screened to minus 35 Tyler mesh. Table 2 shows screen analysis of the various as-ground mattes. It can be seen from this table that the higher S mattes have a much smaller particle size than the low-S mattes. This is because the higher the S level in the matte, the more brittle it becomes, making it easier to grind. The metal extraction was calculated to be the amount of metal taken into solution versus the total amount present in the matte.

Table 1.—Composition of phases[1] in superalloy mattes,[2] weight percent

Phase	Ni	Cr	Co	Fe	Mo	W	Ta	Nb	S
Matte 1	44.3	11.4	6.9	3.9	2.2	0.4	1.0	0.6	25.7
Metallic	67.0	3.4	14.2	10.9	ND	ND	ND	ND	4.5
Ni sulfide	61.9	ND	4.9	1.3	ND	ND	6.3	ND	25.5
Cr sulfide	11.3	29.3	7.1	3.5	ND	ND	11.5	ND	35.4
Subphase 1 . .	8.1	8.0	3.7	1.9	51.8	9.5	15.6	ND	NDt
Subphase 2 . .	4.9	2.7	6.4	1.7	5.9	18.5	57.6	ND	NDt
Matte 2	51.8	11.6	8.5	4.4	2.8	1.1	1.1	.6	15.9
Metallic	70.1	2.7	15.8	7.9	NDt	NDt	ND	NDt	T
Ni sulfide	72.3	ND	4.2	1.2	NDt	NDt	NDt	NDt	22.3
Cr sulfide	11.5	43.8	4.2	ND	NDt	NDt	NDt	NDt	37.9
Subphase 1 . .	2.4	T	ND	ND	19.3	75.6	1.9	T	NDt
Subphase 2 . .	1.8	1.9	ND	ND	42.0	51.6	1.4	T	NDt

ND Not detected.
NDt Not determined.
T Trace.
[1]Phase composition determined by electron microprobe analysis.
[2]Matte composition determined by chemical analysis.

Table 2.—Screen analysis of superalloy mattes according to percentage of sulfur in sample, weight percent of each size fraction

(Samples water-jet granulated except as noted)

Screen size, Tyler mesh	0.0	2.8	4.3	6.9	12.6	15.9[1]	15.9	23.3	25.7	33.7[1]
Plus 35	36.8	21.9	14.0	0	2.3	5.2	0	T	0	0
Minus 35 plus 48	29.4	23.7	22.7	21.5	12.5	16.1	0	0.1	0	T
Minus 48 plus 65	10.8	10.7	12.3	13.1	10.9	9.7	0	.8	0	.2
Minus 65 plus 100	11.7	19.3	23.3	28.3	28.4	17.5	T	27.6	T	19.3
Minus 100 plus 150	4.1	10.3	11.8	14.7	14.0	13.9	.7	17.0	1.3	7.1
Minus 150 plus 200	1.9	6.0	6.7	11.6	15.6	T	42.6	38.3	42.3	18.0
Minus 200 plus 270	1.6	4.0	4.4	5.2	10.8	9.8	40.1	11.0	49.3	38.1
Minus 270 plus 400	.8	1.9	2.7	3.8	4.0	20.5	12.5	3.7	4.2	12.4
Minus 400	2.9	2.2	2.1	1.8	1.5	7.3	4.1	1.5	2.9	4.9

T Trace.
[1]Not granulated.

The leaching studies were conducted on materials with S levels ranging from 2.8 to 33.7 pct and on a metal sample containing no S. The results summarized in table 3 show that as the S level was decreased, the material became more reactive in terms of Ni, Co, Cr, Fe, Al, and Mo extraction. With S levels at approximately 4 pct, over 99 pct of the Ni, Co, and Fe were leached in 3 h, and 85 to 95 pct of the Cr and Mo were leached. The granulated and ground metal with no S was the most reactive material. Essentially all the Ni, Co, Cr, Fe, and Mo were extracted in a 3-h leach time. With increasing S level, less Cr and Mo were extracted, while the Ni, Co, and Fe extractions decreased slightly. Figure 2 illustrates the amount of Ni, Co, and Cr leached in 2 h as a function of the S level in the matte: The very large difference in Cr extraction as the S level changed is apparent. The Mo extraction was approximately midway between the Cr and Co extraction. As described in the previous section, the practical lower limit of S is in the 4- to 7-pct range because of the difficulty in grinding the material, and further studies were conducted on mattes with the S content in this range. If a granulation procedure could be developed that did not require further grinding, metal with no S would be the preferred starting material for leaching.

As mentioned above, Cu ion was added to increase the leaching rate. Table 4 shows the effect of the Cu concentration on the leaching rate of mattes of varying S level. These results show that the low-S mattes did not require the $CuCl_2$ leaching aid to attain rapid leaching rates. Very little difference was found in the leaching rate with or without the Cu. When Cu was added as a leaching aid, its removal from solution was necessary. This was accomplished by the two-stage countercurrent leaching procedure shown in figure 3. In the first stage, no Cl_2 was added to the solution, and free S was added in an amount sufficient to react with the Cu in the solution. This quantitatively precipitated the Cu from solution according to the reactions shown in the next column.

$$Ni_3S_2 + 2Cu^+ + S^o \rightarrow 2NiS + Ni^{2+} + Cu_2S. \quad (E)$$

$$NiS + 2Cu^+ \rightarrow Cu_2S + Ni^{2+}. \quad (F)$$

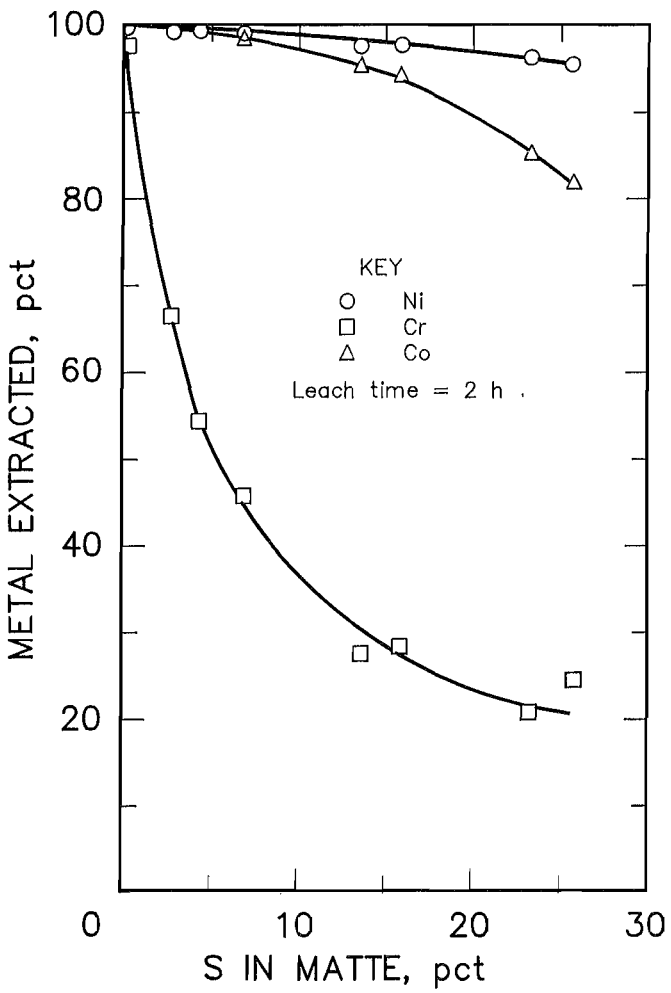

Figure 2.—Metal extraction versus S content in matte.

Table 3.—Results of leaching granulated superalloy mattes at 95° C

Leach time, h	Final ORP, mV	Metal extraction, wt pct				
		Ni	Cr	Co	Fe	Mo
0 pct S—GRANULATED SUPERALLOY						
1	286	62.9	62.9	65.2	73.3	60.6
2	417	99.7	97.6	99.8	99.3	96.9
3	871	~100	98.5	~100	99.4	97.6
2.8 pct S IN MATTE						
1	260	76.2	53.3	76.3	77.6	71.3
2	494	99.6	66.1	99.8	99.4	94.4
3	901	99.9	91.2	~100	99.7	95.6
4.3 pct S IN MATTE						
1	310	86.6	44.5	86.3	88.0	76.0
2	515	99.5	54.1	99.6	99.4	92.1
3	680	99.8	83.2	99.9	99.8	93.5
6.9 pct S IN MATTE						
1	300	89.2	34.6	87.1	89.6	77.8
2	656	99.2	45.4	98.8	98.5	90.6
3	843	99.5	70.3	99.5	99.2	91.6
4	630	99.6	72.6	99.3	99.6	92.6
12.6 pct S IN MATTE						
1	293	95.9	12.8	93.3	95.8	80.9
2	613	97.8	25.9	95.3	97.1	86.2
15.9 pct S IN MATTE						
1	381	96.5	7.5	89.9	94.0	39.1
2	595	98.0	28.4	94.3	96.4	47.4
23.3 pct S IN MATTE						
1	478	90.6	1.0	59.6	69.6	45.4
2	682	96.5	20.8	85.4	85.8	65.6
3	612	96.2	8.6	83.6	83.7	56.1
4	613	96.1	15.5	84.7	84.4	61.5
5	623	95.8	28.5	86.8	79.1	68.6
6	609	97.6	36.5	89.3	86.6	74.6
25.7 pct S IN MATTE						
1	452	89.7	2.8	56.8	70.0	10.3
2	571	95.8	24.7	82.0	86.3	30.4
33.7 pct S IN MATTE[1]						
0.5	399	79.8	0.4	47.5	54.1	9.9
1	560	91.9	1.6	60.7	61.8	13.3
2	637	90.8	9.8	62.0	64.2	21.2
3	658	91.2	19.4	69.3	64.8	25.9

[1]Not granulated.

After solid-liquid separation, the leach solution was sent to the Ni-Co recovery circuit. Spent electrolyte from the Ni-Co electrowinning contacted the residue from the first leach step. In this stage, the Cl_2 was added to the solution. Copper was redissolved and the bulk of the metals was leached in this stage. This solution then was recycled to the first stage, in which some leaching occurred and the Cu was precipitated. The second-stage leach residue was sent to the W, Ti, Ta, and Nb recovery procedure. This two-stage procedure gave essentially the same results as a single-stage leach with the same total retention time.

Table 4.—Effect of copper concentration in leach solution on metal extraction

(1-h leach time, 95° C)

Cu in leach solution, g/L	Final ORP, mV	Metal extraction, wt pct				
		Ni	Cr	Co	Fe	Mo
6.9 pct S IN MATTE[1]						
0	427	98.8	44.7	98.2	98.4	88.9
14.4	515	99.2	42.4	98.6	98.4	91.6
29.0	675	99.1	42.6	98.6	98.4	91.8
42.6	570	99.2	45.5	98.6	98.0	91.6
56.7	656	99.2	45.4	98.8	98.5	90.6
18.9 pct S IN MATTE						
0	375	81.2	10.2	77.0	73.8	42.0
15.3	341	79.1	5.4	77.0	78.2	38.7
30.1	371	87.2	5.9	86.3	90.8	44.7
44.6	371	91.8	6.1	87.4	91.2	51.9
59.6	409	93.9	6.0	88.8	91.8	43.0
33.7 pct S IN MATTE						
0	559	75.0	3.3	57.0	62.0	20.7
14.7	471	88.8	1.3	53.2	59.6	18.5
29.6	483	91.3	1.4	56.8	62.2	18.9
44.5	481	91.9	1.2	58.1	61.9	18.9
59.9	484	92.7	1.4	62.1	61.4	16.1

[1]2-h leach time.

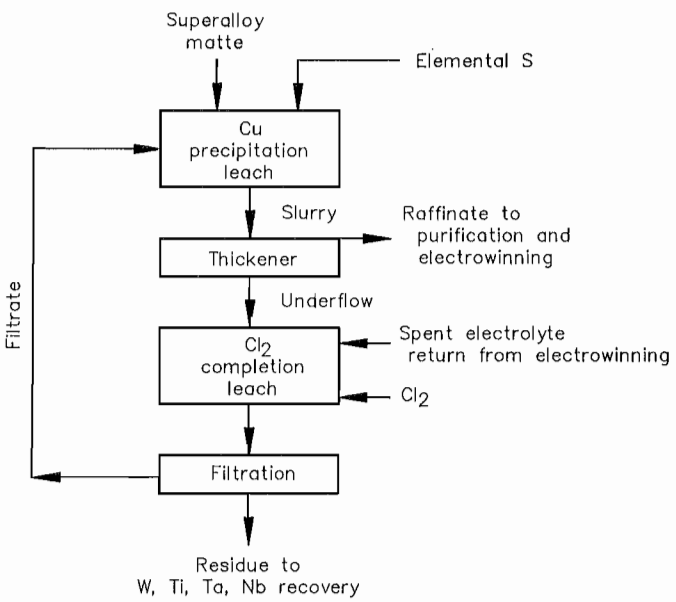

Figure 3.—Two-stage countercurrent leach.

A series of tests was conducted to determine whether any difference existed in leaching characteristics between granulated and nongranulated mattes ground to the same particle size. The results summarized in table 5 show that essentially no difference existed in the metal extractions between granulated and nongranulated mattes for a medium S level (15.9 pct). For a high-S matte (25.7 pct), the Cr, Co, and Fe extractions were significantly greater at 2 h for the granulated matte than for the nongranulated matte. The Ni extraction was essentially the same. Apparently the granulation results in a more porous structure that allows the more difficult-to-leach metals to be more easily extracted in the case of a high S level.

Table 5.—Leaching results for granulated versus nongranulated mattes at 95° C, percent extration

S in matte, pct	Leach time, h	Ni	Cr	Co	Fe	Mo
GRANULATED						
15.9 . .	1	96.5	7.5	89.9	94.0	39.1
	2	98.0	28.4	94.3	96.4	47.4
25.7 . .	1	89.7	2.8	56.8	70.0	10.3
	2	95.8	24.7	82.0	86.3	30.4
NONGRANULATED						
15.9 . .	1	93.6	6.2	87.9	92.6	50.8
	2	97.4	24.9	91.5	94.9	73.8
25.7 . .	1	91.9	1.6	60.7	61.8	13.3
	2	90.8	9.8	62.0	64.2	21.1

As described previously, the higher S matte allowed a more selective leach between the Ni-Co and Cr-Fe. A matte with 20 to 25 pct S resulted in extraction of over 90 pct of the Ni and Co in 3 h, leaving most of the Cr and some of the Fe and Mo in the residue. Up to 92 pct of the Cr and Mo and 99 pct of the Fe could then be removed from the residue by releaching with fresh leach solution in two additional 2-h cycles. The Cu leaching aid needed a concentration of at least 40 g/L to obtain these results. Although greater selectivity was obtained with the high-S mattes, the first leach solution still contained Cr and Fe that had to be removed in a precipitation step, and the Cu leaching aid had to be removed with a two-stage leach. For these reasons, the researchers thought that the most practical approach would be to use a low-S matte and take all the Cr and Fe into solution initially and remove it in a single step, instead of processing two leach solutions. Also, the Cu leaching aid would not be needed, eliminating the two-stage leach. A typical pregnant leach solution composition obtained from a 3-h leach of a 4- to 7-pct-S matte was as follows (in grams per liter): 112 Ni, 7.2 Cr, 8.4 Co, 6.2 Fe, 1.4 Mo, 0.46 W, and 0.07 Al (starting with 80 g/L Ni in the leach solution).

SOLVENT EXTRACTION

Previous studies by Brooks (*2*) showed that trioctyl phosphate diluted in kerosene effectively extracts Mo. A leach solution with the concentration mentioned at the end of the "Leaching Studies" section was contacted with 25 vol pct trioctyl phosphate in kerosene. Equal volumes of organic and aqueous solutions were used. Two contacts with the organic solution decreased the Mo concentration from 1.40 g/L to less than 0.001 g/L and Fe concentration from 6.2 to 2.0 g/L. The Mo and Fe were stripped from the organic with 0.3*M* HCl. Testing also revealed that the ORP of the final leach solution fed to the solvent extraction must be at least +650 mV (Pt versus Ag-AgCl) to extract all of the Mo and most of the Fe. Apparently, at a lower ORP some of the Mo is in a lower valence state and can not be extracted by the organic. Table 6 and figure 4 show these results for Mo, Fe, and W extraction

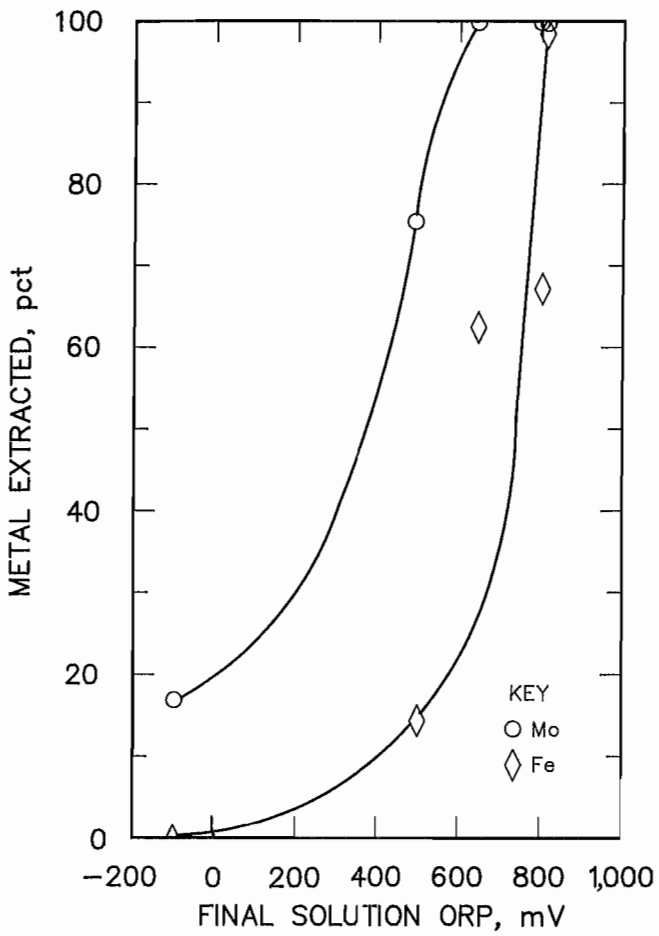

Figure 4.—Solvent extraction of leach solution.

from leach solutions of varying final ORP. No difficulties were encountered with phase separation. Limited testing was conducted on this aspect of the process, however. One problem that was not addressed was that some W was extracted with the Mo and Fe, and the W was not stripped from the organic with the HCl strip solution. Whether this W could be removed by some other method was not investigated.

Table 6.—Solvent extraction of leach solution—percentage of metals extracted versus final solution ORP

(Conditions: 25 vol pct trioctyl phosphate in kerosene, two contacts with equal volumes aqueous and organic, starting solution in grams per liter: 1.41 Mo, 6.20 Fe, 0.46 W)

Final sol ORP, mV	Mo	Fe	W
-100	17.0	0.3	54.4
+500	75.9	15.0	97.0
+650	~100	63.4	~100
+800	~100	68.1	94.4
+820[1] ...	99.7	99.6	73.3

[1]Starting solution in grams per liter: 1.84 Mo, 3.30 Fe, 0.03 W.

CHROMIUM AND IRON RECOVERY

Precipitation tests to remove Cr and Fe were conducted on raffinates generated in the solvent extraction studies. An NaOH solution was added to the raffinate to increase the pH to precipitate Cr and Fe. Initial tests conducted at 100° C resulted in a poor separation. As shown in figure 5, complete removal of the Cr and Fe could not be obtained without also removing 10 to 20 pct of the Ni and Co. This was not an acceptable procedure, especially since the Ni was the major component in solution. In addition, the precipitate obtained under these conditions was very difficult to filter, as expected, and trapped a considerable amount of leach solution in the filter cake.

A more satisfactory procedure was to add the NaOH solution and then heat the solution to 200° C in an autoclave. This resulted in a much greater separation of Cr-Fe from the Ni-Co. In addition, the precipitate was much easier to filter. One hour at 200° C produced a satisfactory precipitate. To control precipitation, varying the amount of NaOH added as a function of the amount of metals in the solution was found to be a better method than adjusting the pH to a specific value. Figure 5 illustrates the amount of metals precipitated as a function of the amount of NaOH added for a specific leach solution

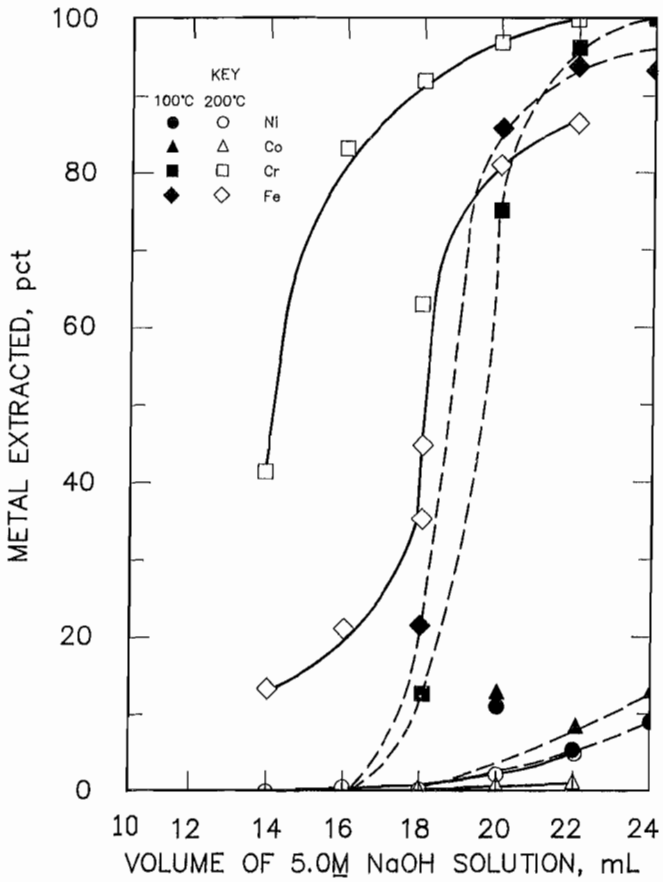

Figure 5.—Metals precipitated versus amount of NaOH added.

at both 100° and 200° C. After 22 mL of 200-g/L NaOH solution was added to 75 mL of leach solution (containing 7.3 g/L Cr and 3.9 g/L Fe) and the solution was treated at 200° C, 100 pct of the Cr, 86 pct of the Fe, and less than 5 pct of the Ni and Co were removed. Metals would be recovered from the precipitate by calcining the material, then reducing it to metallic ferrochrome using Al or some other suitable reductant. A pure Cr metal could be recovered from the ferrochrome using existing technology, if Cr was the desired product (*13*).

NICKEL AND COBALT RECOVERY

In this study, the purified leach solution containing the Ni and Co was not processed to recover the metals. Since this solution was essentially the same as the purified leach solution used in the Falconbridge process (*14*) described earlier, it was thought that it was not necessary to process this solution further. The Falconbridge process uses SX-EW to recover pure Co and Ni. The leach solution is given several purification steps, then the Co is separated from the Ni by solvent extraction. The Co strip solution

from the solvent extraction is purified further by precipitation and ion exchange and then is sent to electrowinning cells to recover the Co. The Ni raffinate from the Co solvent extraction is directly electrowon. The Ni concentration in the raffinate is reduced from 230 to 85 g/L before it enters the electrowinning cell. The spent anolyte from the electrowinning contains approximately 54 g/L Ni. This solution then is recycled to the beginning of the process to leach more matte.

LEACH RESIDUE

The residue from the chloride leach contains W, Ta, Ti, and Nb. In addition, the chloride leach of the matte generates both sulfate ion in the leach solution and free S in the residue. The free S in the residue can be recovered and recycled by leaching with hot perchloroethylene. The solubility of S in this solvent is very temperature dependent. The solubility at 25° C is 25 g/L, while the solubility at 100° C is 422 g/L (*15*). Leaching the residue at 100° C and then allowing the solvent to cool results in the precipitation of the free S from the residue. An alternate procedure for S removal is the method described by Herve (*16*). This procedure uses different solvents, such as 1,2,ethanediol; 1,2-propanediol; 2-(2-methoxyethoxy)ethanol; 2-(2-ethoxyethoxy)ethanol; or 2-(2-butoxyethoxy)ethanol, to dissolve the S from the leach residue. The residue is leached hot and then the solvent is cooled to precipitate the S in a manner similar to the perchloroethylene treatment.

The amount of sulfate ion formed during the leaching seemed to be somewhat erratic. Problems that this might generate in the various solvent extraction steps, as well as the effect on leaching as the sulfate ion builds up in the recycle streams, were not addressed, and a suitable method to precipitate the sulfate ion from solution, such as barite ($BaSO_4$) precipitation, was not developed.

The W remaining in the residue was removed by oxidizing the residue in air at 800° C, followed by leaching with 400 g/L NaOH solution. The W was recovered as an oxide by evaporating the solution. The residue from the W recovery step contained the Nb, Ta, and Ti.

CONCLUSIONS

The results of this study show that the individual metals in mixed superalloy scrap can be recovered by a matte-smelting, hydrometallurgical procedure. The mixed scrap was converted to a matte by adding S directly to the molten metal. This matte was then granulated and ground to a minus 35-mesh particle size and was leached with an $HCl\text{-}Cl_2$ leach solution. The effect of S content on the leachability of the matte was investigated, and it was found that the lower the S level, the more easily the material leached. Granulated and ground metal with no S leached best, but was very difficult to grind to a suitable particle size. Mattes with S levels less than 4 pct also were very difficult to grind. A S level in the matte of 4 to 7 pct provided the best combination of ease in leaching and grinding. This leaching process took essentially all the Ni, Co, Cr, Fe, and Mo into solution in a 3-h leach. The Mo was recovered by solvent extraction, and the Cr and Fe were recovered together by precipitation. The Ni and Co could be recovered as pure individual metals by a commercial SX-EW procedure.

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